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(54) Process for improving the
combustion of gas oils

(57) This process consists in adding to
gas oil from 100 to 5000 ppm of
water in the form of a micellar clear

and limpid solution, which is stable for
long times, obtained by the addition of
one or more surfactants, associated
with one or more auxiliary surface-
active agents (co-surfactants).

This invention substantially
improves the combustion of gas oils.

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SPECIFICATION

Process for improving the combustion of gas oils

This invention relates to a process of improvement of the properties of combustion of gas oils, by the addition to the gas oil of appropriate quantities of water and one or more surfactants, associated if required with one or more co-surfactants, the latter being compounds capable of forming hydrogen bonds with water. The gas oil treated according to the invention has a completely clear and limpid appearance, the water being completely solubilized and not separating.

It is known to utilize organometallic salts of Ca^{++} , Ba^{++} , Mn^{++} , Fe^{+++} and others to improve the combustion of gas oils. Such additives, incorporated in gas oils in amounts of the order of 10 to 1000 ppm, allow reduction in the emission of soot, solid residues, CO and combusted hydrocarbons, by initiating the formulation of free radicals. However, these additives have a certain number of disadvantages, notably toxic emissions at the exhaust point, particularly in the case of salts of Ba^{++} , and in general formation in combustion chambers of metal oxides which can exert an abrasive action.

The beneficial effect of water on the combustion of hydrocarbons is known. For instance, it was proposed in 1954, in French Patent Specification 1 100 551, to incorporate into liquid fuels small quantities of water in the presence of emulsifying agents, for example condensation products of fatty alcohols, phenols or fatty acids with ethyl oxide. However, in practice, stable emulsions are not obtained and the incorporated water separates with time, leading to disadvantages in storage reservoirs, such as corrosion and bacterial growth. Moreover, the water droplets become entrained in filters and cause swelling and distortion, yielding unexpected blockages of the supply from the reservoir, clogging of pumps, etc. The presence of drops of water causes the formation of ice crystals in cold weather, giving frosting and blockage of the filters in the supply circuit to the engine.

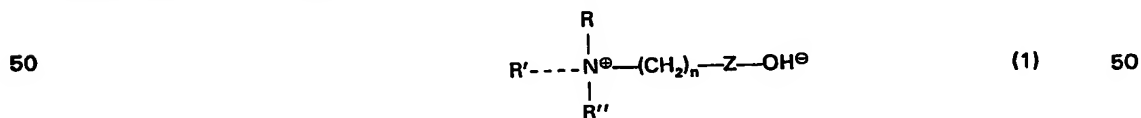
More recently, attempts have been made to remedy deficiencies of the prior art, by the utilization of special mixtures of surfactant compounds, thus giving stable emulsions containing water in the form of very fine particles dispersed in the hydrocarbon. For instance, U.S. Patent Specification 3 876 391 describes the incorporation of 6% to 16% of water into motor fuel in the presence of 3% to 8% of a fatty acid ester, possibly polyethoxylated, and including an amine, polyethoxylated alkyl-phenol, polyethoxylated fatty acid amide or polyethoxylated sorbitol fatty ester surfactant; moreover, it is necessary to add 0.5% to 10% of a water-soluble amide or amine, for example, acetamide, formamide, monoethanolamine, ethylene-diamine etc. The proposed solution is thus notably complex.

The problem has thus remained complicated throughout recent years, as can be seen from U.S. Patent Specification 4 083 698, which still recommends mixtures of fatty acid salts with non-ionic polyethoxylated surfactants, in order to obtain very fine stable emulsions containing 0.1% to 10% of water and 1% to 10% of a lower alcohol in a fuel. When the latter is relatively heavy, in particular a diesel fuel, that is to say a gas oil, the proposed combination is no longer generally sufficient and the patent explains (columns 24 and 25) that it is necessary to add up to about 15% of cyclohexanol and/or cyclohexanone.

The present invention provides a marked improvement in this technique, in that it permits a considerable improvement in the combustion of fuels of the gas oil type, that is to say hydrocarbons boiling between about 200° and 425°C , in a particularly simpler and more economical manner, which can be more readily carried out than the known technique.

This invention results from two unexpected discoveries: 1. The desired improvement of a gas oil can be obtained by the incorporation of low proportions of water, namely from 0.01% to 0.5%, contrary to the several percent utilized in the prior art; 2. the water is capable of being put into an emulsion which is completely clear and very stable by means of certain specific surfactant compounds, which have never been employed for this purpose in the past.

The new process according to the invention which consists in emulsifying 100 to 5000 parts per million of water in gas oil in the presence of a surfactant, is characterized in that the surfactant is constituted by one or more compounds of the formula:



where Z represents CO or SO_2 , n is an integral number from 1 to 6, R is an alkyl group or a hydrogen atom, R' is an alkyl or alkenyl group, a hydrogen atom or an acyl group, while R'' can be a methyl group, but can also be absent.

When R is an alkyl group, it contains 1 to 30 carbon atoms and preferably 1 to 4. If R' is an alkyl or alkenyl group, it can contain 1 to 30 carbon atoms, preferably 1 to 18. If R' is an acyl group, R''-CO-, its number of carbon atoms generally is from 2 to 18, that is to say R'' is C_1 to C_{17} ; preferably, R'' is a C_{17} aliphatic chain.

In the embodiment of the invention, the surfactant compounds according to formula (1) are N-

alkyl-dimethyl-glycines or N-alkenyl-dimethyl-glycines, namely betain derivatives in which R and R' are methyl groups, R' is a C₆ to C₁₈ and, preferably, a C₁₀ to C₁₈ aliphatic chain, n is 1 and Z represents CO. These agents can be represented by the formula:



- 5 In particular, R' is a decyl, undecyl, dodecyl, tetradecyl, hexadecyl, octadecyl or octadecenyl group. The amphoteric compounds (2) can be employed in the form of salts of anions connected to the



or cations combined with —COO⁻; the cations can for example be alkali metals, ammonium metals, ammonium or amines.

- 10 According to another embodiment, the compounds of formula (2) carry a sulphonic group —SO₃⁻ in place of —COO⁻.

The surfactant agents according to the invention can also be constituted by taurine

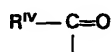


or by a salt of this compound attached to the NH₂ or the SO₃H group.

- 15 Another important series of surfactant agents for carrying out the invention comprises compounds of the formula (1), in which R' is an aliphatic acyl group, R^{IV}—CO, while R'' is absent. R is preferably C₁ to C₄. Typical products of this series are the N-acyl sarcosinates of alkali metals (M).



Preferably, the



acyl group is derived from a C₆ to C₁₈ fatty acid, particularly caproic, caprylic, capric, lauric, myristic, palmitic or stearic or, if required, unsaturated acids, such as oleic, linoleic or linolenic acids.

- 25 It is advantageous to employ the agents (4) in the form of mixtures comprising acyl groups having different numbers of carbon atoms, corresponding to several fatty acids derived from a natural oil or grease. For example, using coprah (coco) oil, a mixture of compounds (4) where the R^{IV}CO groups are C₈, C₁₀, C₁₂, C₁₄, C₁₆ and C₁₈ (oleic), with lauric (approximately 44%) and myristic (approximately 18%) acyl groups predominating, can be used.

- 30 Preferably, the invention is carried out by also employing a co-surfactant of a type known per se for this kind of emulsion, for example an alcohol, an amine or an amide. Lower alcohols, such as methanol, ethanol, propanol, isopropanol and the butanols, are generally very suitable.

The proportion of co-surfactant, like the surfactant itself, is of the order of 10 to 5000 ppm and particularly 25 to 2000 ppm or 0.0025% to 0.2% of the gas oil. Depending on the choice made, the weight of the co-surfactant is generally from 0.1 to 1 part, usually 0.5 to 1 part, per 1 part of the surfactant by weight.

- 35 The quantity of the surfactant utilized is proportional to the quantity of water to be solubilized. In a general manner, aromatic gas oil having an aromatic content higher than 25% require smaller quantities of surfactant than paraffinic gas oils having an aromatic content of the order of 10% to 15%.

The addition of the surfactant, if required in association with the co-surfactant, allows the water/gas oil interfacial tension to be substantially diminished by a value of the order of 30 to 40 dynes cm^{-1} .

The system obtained has the form of a liquid dispersion in which the continuous external phase is the gas oil, while the disperse phase is constituted by the water in droplets or spherules having a diameter lower than 0.4 micron. The entire dispersion has an appearance which is transparent to light. The system formed is thermodynamically stable and, contrary to known emulsions, the water does not separate, even after a very long time of the order of several months.

In a general manner, the process of the invention is carried out by the addition to the gas oil of 100 to 5000 ppm of water, 10 to 5000 ppm of the co-surfactant compound, the weight ratio of the latter to the surfactant being from 0.1 to 1. However, very good results can be obtained with 100 to 1000 ppm of water and 25 to 2000 ppm of the surfactant, accompanied by 0.5 to 1 part by weight of the co-surfactant compound.

The non-limitative examples which follow illustrate the invention in various forms with specific surfactants.

In these examples, a diesel engine was operated with gas oil containing no additive and, on the other hand, with gas oils treated according to the invention.

A gas oil was used having the following characteristics:

	— relative density at 15°C with respect to water at 4°C	0.831	
20	— 50% distillation point	255°C	20
	— 90% distillation point	363°C	
	— Final distillation point	340°C	
	— Viscosity at 20°C	4.1 cst	
	— Initial water content	75 ppm	

The water utilized was de-mineralised.

The vehicle employed for the tests was placed on a dynamometric chassis. The location in which the tests were to be carried out was climatically controlled, such that it was possible to place it under completely known and reproducible conditions (20°C). The procedure began with a first stage having a test time of 45 mins., at a stabilized speed, the engine operating at two-thirds of its nominal power output. The vehicle tank contained the gas oil for the tests. The tests were carried out when a good thermal equilibrium of the engine had been obtained.

A substantially similar operative mode has also been carried out on an engine on a test bench.

The tests were conducted in accordance with the conditions of the Journal Officiel de la République Française for the registration of vehicles by the EEC, namely:

— Tests at constant speed: with the engine being supplied with plain fuel, the measurements effected were divided in a uniform manner between a regime corresponding to the maximum power of the engine and the greater of the following regimes: (1) 45% of the rate of rotation corresponding to maximum power and (2) 1000 revs per minute.

— Free acceleration tests: the gearbox of the engine was placed in neutral and the engine was connected up; with the engine turning slowly, its accelerator was operated rapidly but carefully, in such a manner as to obtain the maximum throughput of the injection pump; this position was maintained until the governor operated; when this speed was obtained, the accelerator was relaxed until the engine resumed its slow speed.

The operation was repeated at least six times in order to sparge the exhaust system and, where necessary, the apparatus was then calibrated.

The measurements consisted in determining the opacity of the fumes recovered from the vehicle exhaust. The apparatus used was an opacimeter of the type and mode of utilization conforming to the description published in the Journal officiel de la République Française of 21st March 1974, Annexes 7 and 8.

The test vehicle was equipped with 3.3 litre capacity engine developing a power of 56 Kw at 3200 revs per min.

EXAMPLES 1 to 7

Tests on the engine stabilized at 1500, 2000, 2500 and 3200 revs per min. were effected, on the one hand with the gas oil without additive and on the other hand with the various additives indicated in the results Table I.

The latter are expressed as the coefficients of adsorption in m^{-1} found for the exhaust gases, following measurement of the opacity mentioned above.

Each result is the average of 4 determinations, the variation not exceeding 5%. The percentage reduction of the adsorption coefficient is designated as "improvement," in each case, with respect to the coefficient found for the gas oil not containing any additive. Thus in the column for 1500 revs per min. in Table I, between Examples 1 and 2, the improvement of 17.5% results from the calculation

$$100 \times (1.94 - 1.60) : 1.94 = 34 : 1.94 = 17.5\%.$$

The surfactant agent utilized in Examples 2 to 4 is constituted by a mixture of sodium N-acyl-sarcosinates of the formula (4) given above, which contain acyl groups $R^{IV}-CO$ derived from coprah (coco) oil fatty acids.

By way of comparison, tests were also effected with, as additives, barium sulphonate (Examples 5 and 6) and a standard surfactant based on polyoxyethylated alcohols (UKANIL 36 manufactured by Société Péchiney-Ugine-Kuhlmann).

TABLE I
Coefficients of adsorption (C) in m^{-1}
and % Improvement (A)

No.	Additive	1500 r/m C A	2000 r/m C A	2500 r/m C A	3200 r/m C A
1	None	1.94	1.47	2.61	4.45
2	Sarcosinate 25 ppm Water 100 " Butanol-2 25 ppm Improvement	1.60 17.5%	0.90 38.8%	1.80 31%	3.60 19.1%
3	Sarcosinate 500 ppm Water 1000 ppm Butanol-2 500 ppm Improvement	1.50 22.7%	1.10 25%	1.75 33%	2.90 34.8%
4	Sarcosinate 2000 ppm Water 5000 " Butanol-2 2000 " Improvement	1.55 20%	1.00 32%	1.90 27.2%	3.25 27%
5	Ba Sulphonate 50 ppm Improvement	1.45 25.2%	1.00 32%	2.00 23.3%	4.1 7.8%
6	Ba Sulphonate 100 ppm Improvement	1.40 27.8%	0.95 35.4%	1.50 42.5%	3.50 21.3%
7	Polyoxyeth. alcohols 600 ppm Water 1000 ppm Butanol-2 600 ppm Improvement	1.70 12.3%	1.35 8.2%	2.20 15.7%	3.70 16.8%

The overall average improvements in percentage thus were:

- 26.6% for the sarcosinate of Example 2
- 28.8% for the sarcosinate of Example 3
- 25.3% for the sarcosinate of Example 4
- 22.0% for 50 ppm of sarcosinate of Example 5
- 31.0% for 100 ppm of sarcosinate of Example 6
- 13.2% of the polyoxyethylated alcohols of example 7

It will be seen that the sarcosinate gives results comparable with those obtained with the organic barium compound, without giving the disadvantages, and better than those of polyoxyethylated alcohols utilised in the prior art.

It also appears in the light of Examples 2 to 4 that 1000 ppm of water can suffice to give an optimum overall improvement.

EXAMPLES 8 to 12

Free acceleration tests.

The same sarcosinate as in the foregoing Examples 2 to 4.

TABLE II

No.	Additive	Coefficient of adsorption in m^{-1}		Improvement
		with additive	Control test without additive	
8	Sarcosinate 500 ppm Water 1000 " Butanol-2 500 " }	0.95	1.18	19.5%
9	Sarcosinate 2000 " Water 5000 " Butanol-2 2000 " }	0.80	1.16	31.0%
10	Diethyl-Ba 50 "	0.94	1.22	22.9%
11	" " 100 "	0.79	1.39	43.1%
12	Polyoxy-ethylene alcohols (UKANIL 36) 600 ppm }	1.01	1.09	7.4%

It can be seen that at the same free acceleration the improvements due to the sarcosinates are of the same order as those due to barium sulphonate and higher than those given with polyoxyethylated alcohols.

EXAMPLES 13 AND 14

In the manner described in connection with Examples 1 to 7, using a stabilized regime, gas oils containing water were tested in the presence of N-lauryl-dimethyl-glycine, that is to say a betain corresponding to formula (2) given above where R' is a dodecyl group. To calculate the improvements, the figures of Example 1 relating to the gas oil without additive are repeated in Table III on the following page.

TABLE III

Coefficients of adsorption (C) in m^{-1}
and % improvements (A)

No.	Additive	1500 r/m		2000 r/m		2500 r/m		3200 r/m	
		C	A	C	A	C	A	C	A
1	None	1.94		1.47		2.61		4.45	
13	Betain 500 ppm Water 1000 " " Butanol-2 500 " " Improvement	1.60	17.5%	1.30	11.5%	1.80	31%	3.40	23.6%
14	Betain 2000 ppm Water 5000 " " 3-Methyl butanol-1 2000 ppm Improvement	1.35	30.4%	0.80	45.5%	1.30	50%	2.90	34.8%

The overall average improvements amount to 20.9% for Example 13 and 40% for Example 14. Comparison with Table I shows that, for 500 ppm of surfactant and 1000 ppm of water, the sarcosinate is more effective than the betain, while at a rate of 2000 ppm of surfactant and 5000 ppm of water, in contrast, the betain gives the better results. Thus, the invention allows a choice of the most appropriate emulsifying agent depending upon the proportion of water to be incorporated into the gas oil. The combined use of a sarcosinate with a betain is also recommendable.

EXAMPLES 15 AND 16

The surfactant, N-lauryl-dimethyl-glycine, of Examples 13 and 14 was tested under free acceleration, in parallel to control tests with the same untreated gas oil. The following adsorptions in m^{-1} were found:

treated gas oil:	Example 13	Example 14
	0.98	0.90
Gas oil without additive:	1.21	1.17
improvement	19%	23%

In the following Examples, the surfactants employed are compounds of formula (3), in which the NH_2 group is replaced by an aliphatic or alkaryl hydrocarbon chain, which can carry carboxylic groups, in particular sulpho-succinic groups. The sulpho group in these compounds is neutralized by an alkaline or nitrogen-containing base.

EXAMPLES 17 TO 19

The surfactant employed is a sodium alkyl-aryl-benzene-sulphonate of the sodium lauryl-benzene-sulphonate type, known commercially under the name SYNACTO 406, produced by Esso. The results are given in Table IV.

TABLE IV
Coefficients of adsorption (C) in m^{-1}
and % Improvements (A)

No.	Additive	1500 r/m		2000 r/m		2500 r/m		3200 r/m	
		C	A	C	A	C	A	C	A
1	None	1.94		1.47		2.81		4.45	
17	SYNACTO 25 ppm Water 100 " Isopropanol .25 " Improvement	1.20	38%	0.9	39.4%	1.90	27.2%	3.7	16.9%
18	SYNACTO 500 ppm Water 1000 " Isopropanol 500 " Improvement	1.45	25.2%	1.00	32%	2.05	21.3%	3.40	23.8%
19	SYNACTO 3000 ppm Water 5000 " Isopropanol 2000 " Improvement	1.20	38%	0.80	45.5%	1.85	29%	3.30	25.8%

EXAMPLES 20 TO 21

The same gas oils treated as in Examples 17 to 19, that is to say with a sodium alkyl-aryl-sulphonate surfactant, were tested under free acceleration. The following results were found:

5	Gas oil treated according to example	<u>17</u>	<u>18</u>	<u>19</u>	5
	Coefficient of adsorption	0.86	0.90	0.80	
	Coefficient of gas oil				
	without additive	<u>1.27</u>	<u>1.12</u>	<u>1.17</u>	
10	Improvement	0.41	0.22	0.37	10
	=	32.3%	19.6%	31.6%	

EXAMPLE 22

Tests under stabilized regimes were effected with a gas oil in which 1000 ppm of water and 500 ppm of isobutanol had been emulsified with the aid of 500 ppm of a surfactant constituted by petroleum sulphonates known under the names of PETROSTEP 465 (55%) and PETROSTEP 500 (45%) sold by Stepan.

The results obtained were:

Coefficients of adsorption					
	Regime Revs/ min	Gas oil without additive	Gas oil according to the invention	Improvement	
5	1500	1.94	1.50	22.6%	5
	2000	1.47	1.10	25.2%	
	2500	2.61	2.10	19.5%	
	3200	4.45	3.80	14.6%	
10			Average	20.5%	10

EXAMPLE 23

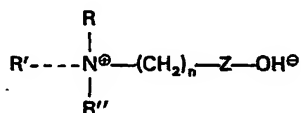
On replacing the Petrostep sulphonates in Example 22 by a mixture of two or other petroleum hydrocarbon sulphonates, sold under the respective marks TRS 16 (70%) and TRS 18 (30%) by Witco, the following improvements were found under the same conditions:

15	17.5%	15
	32.0%	
	29.0%	
	19.1%	
	—	
	average 24.4%	

20 Under free acceleration, the same gas oil gave an improvement of 20.6%. 20

CLAIMS

1. A process of manufacture of a combustible composition, which comprises incorporating into a gas oil 5000 ppm of water and at least one surfactant of the formula:



25 wherein Z represents a CO or SO₂ group, n is an integral number from 1 to 6, R is a hydrogen atom or an alkyl group, R' is a hydrogen atom, an alkyl group, an alkenyl group or an acyl group and R'' is either a methyl group or is absent. 25

2. A process according to claim 1, wherein R is a C₁ to C₃₀ alkyl group.

3. A process according to claim 2, wherein R is a C₁ to C₄ alkyl group.

30 4. A process according to any preceding claim, wherein R' is a C₁ to C₃₀ alkyl or alkenyl group. 30

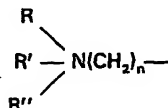
5. A process according to claim 4, wherein R' is a C₁ to C₁₈ alkyl or alkenyl group.

6. A process according to any preceding claim wherein R' is an aliphatic acyl group containing 2 to 18 carbon atoms.

7. A process according to claim 6, wherein the or each surfactant is an alkali metal N-acyl sarcosinate. 35

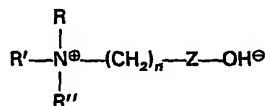
8. A process according to any preceding claim, wherein the or each surfactant comprises an N-alkyl (or N-alkenyl) dimethyl-glycine in which R' is a C₈ to C₁₈ aliphatic chain.

9. A process according to any preceding claim, wherein the or each surfactant is an alkali metal sulphonate in which the group:



is an aliphatic or alkyl-aryl hydrocarbon chain.

- 5 10. A process according to claim 9, wherein the or each surfactant is an alkali metal sulphasuccinate. 5
11. A process according to any preceding claim, wherein the amount of surfactant incorporated into the gas oil comprises 10 to 5000 ppm with respect to the gas oil.
- 10 12. A process according to claim 11, wherein 100 to 1000 ppm of water and 25 to 2000 ppm of surfactant are incorporated into the gas oil. 10
13. A process according to any preceding claim, wherein a co-surfactant comprising an amine, an amide or an alcohol is also incorporated into the gas oil.
14. A process according to claim 13, wherein the co-surfactant is a C₁ to C₆ alcohol.
- 15 15. A process according to claim 13 or 14, wherein the amount of co-surfactant is 0.1 to 1 part by weight per part of surfactant. 15
16. A process according to claim 15, wherein the amount of co-surfactant is 0.5 to 1 part by weight per part of surfactant.
17. A process according to any preceding claim, wherein the water is dispersed in the gas oil as particles of dimensions below 0.4 micron.
- 20 18. A process according to claim 1, substantially as described with reference to the foregoing Examples. 20
19. A combustible composition, when made by a process according to any preceding claim.
20. A gas oil composition comprising hydrocarbons boiling between 200° and 425°C and containing 100 to 5000 ppm of emulsified water and 10 to 5000 ppm of a surfactant which
- 25 corresponds to the formula: 25



wherein Z represents a CO or SO₂ group, n is an integral number from 1 to 6, R is a hydrogen atom or an alkyl group, R' is a hydrogen atom, an alkyl group, an alkenyl group or an acyl group and R'' is either a methyl group or is absent.

- 30 21. A composition according to claim, 20, wherein the water is in the form of particles having dimensions less than 0.4 micron. 30
22. A composition according to claim 20, substantially as hereinbefore described.